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Characteristic intervals in suspension polymerisation reactors: An experimental and modelling study

Fatemeh Jahanzad[a], Shahriar Sajjadi[b], Brian W. Brooks[a,*]

[a]Department of Chemical Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK
[b]Division of Engineering, King's College London, London, WC2R 2LS, UK

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Abstract

Suspension polymerisation of methyl methacrylate was carried out as a model to elaborate on the evolution of particle size average and distribution in the course of polymerisation. Four characteristic intervals in the evolution of particle size were identified as: transition, quasi-steady-state, growth, and identification stages. The effects of stabiliser and initiator concentrations, monomer hold up, reaction temperature, and agitation speed on the characteristic intervals, as well as the kinetics of polymerisation, were examined. The transition stage, which has been totally ignored in the literature, was found to have significant effect on the evolution of particle size. The transition stage is shortened by increasing the rate of polymerisation in the drops (either by increasing initiator concentration or using a higher reaction temperature). Increasing the impeller speed and stabiliser concentration will also lead to a shorter transition period. However, the delayed adsorption of the stabiliser on the surface of drops will prolong the transition stage. It is shown that the occurrence of the quasi-steady state depends on the polymerisation conditions. The quasi-steady state occurs only if the balance between drop break up and coalescence can be maintained. This requires a high rate of drop break up within a period of time during polymerisation (i.e., a low rate of polymerisation in the drops by using a low initiator concentration and reaction temperature, a high agitation speed and a high stabiliser concentration). The mechanisms underlying the growth stage are explained in terms of the overall rates of drop break up and coalescence in the course of polymerisation reactions. It is also shown that the onset of growth stage cannot be defined in terms of a critical conversation or viscosity, and it depends on the polymerisation conditions including mixing. The growth stage occurs if drops are not sufficiently stable against both break up and coalescence. The onset of the growth stage is advanced with a decrease in the rate of drop break up (e.g., decreasing agitation speed and stabiliser concentration). The growth stage can be totally eliminated from a polymerisation process if dispersions with a static steady state can be formed. That requires a high concentration of stabiliser, or a low concentration of monomer, to be used. A population balance model, which included the transition stage and the delayed adsorption of the stabiliser, was developed that is capable of predicting the evolution of drop size in the suspension polymerisation.

Keywords: Suspension polymerisation; Characteristic intervals; Break up; Coalescence; Particle size; Population balance modelling; Methylmethacrylate

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1. Introduction

Suspension polymerisation is widely used in industry to produce high value-added particulate products such as chromatographic separation media, ion exchange resins and supports for enzyme immobilisation. For all these products the average particle size and the breadth of the particle size distribution are two of key factors to guarantee the quality of the product. In comparison with the number of studies appearing in the literature on the kinetics of polymerisation and/or properties of final polymer particles, less attention has been paid to the study of evolution of particle size and particle size distribution. The main reason for this is perhaps the complexity of the phenomena that determines particle size.

In principle, a balance between the rate of drop break up and coalescence determines the size of drops in suspension

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* Corresponding author. Tel.: +44 1509 222 510; fax: +44 1509 223 923.
E-mail address: b.w.brooks@lboro.ac.uk (B.W. Brooks).

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polymerisation. Therefore, the drop size is a strong function of several parameters such as densities and viscosities of continuous and dispersed phases, interfacial tension, type and concentration of suspending agent, dispersed-phase hold up, type of impeller and stirring speed, as well as the kinetics of polymerisation. Suspension polymerisation reactions generally produce particles with a broad or bimodal size distribution. Bead particles, which are the intended product from a suspension polymerisation, with diameters in the range of 10 μm to 5 mm, are usually accompanied with unintended smaller particles. Many aspects of suspension polymerisations have been reviewed in the literature (Brooks, 1990; Dowding and Vincent, 2000; Vivaldo-Lima et al., 1997).

When two immiscible phases are brought into contact by agitation, drops are formed and their size depends on many variables including the agitation speed. An increase in the agitation speed enhances the rate of drop break up and thus favours the formation of smaller drops. However, at very high agitation speeds the drop size may increase with agitation speed due to an increase in the rate of coalescence because of the very large surface area of drops and reduced effectiveness of the suspending agent molecules on the interface. A U-shape dependence of the mean drop size on the agitation speed has been reported by several investigators (Chatzi and Kiparissides, 1994; Johnson, 1980; Zhou and Kresta, 1998). Yang et al. (2001) applied a variable agitation-speed method during the suspension polymerisation of styrene to limit the drop size enlargement during the growth stage and to control the final polymer particle size.

One of the crucial factors in the control of particle size in suspension polymerisation reactors is the type and the concentration of the stabiliser(s) used. The majority of stabilisers used in this process are either water-soluble polymeric materials or inorganic particles. Suspending agents adsorb at the monomer/water interface and, thus, enhance the stability of drops against coalescence. Water-soluble stabilisers also facilitate the drop break up by reducing the interfacial tension. Partially hydrolysed poly vinyl acetate or poly vinyl alcohol (PVA) is one of the polymeric water-soluble stabilisers used in suspension and emulsion polymerisation processes. A number of studies have been reported on the suspension polymerisation with PVA as stabiliser (e.g., He et al., 2002; Konno et al., 1982; Mendizabal et al., 1992; Zerfa and Brooks, 1998). It has been shown that the best PVA grade for using as a stabilising agent in suspension polymerisation is the one with a degree of hydrolysis of 80–90% and molecular weight of above 70,000 (Castellanos et al., 1991; Mendizabal et al., 1992). This grade of PVA forms a thicker and stronger layer on the water/monomer interface and has less tendency to be desorbed. Using PVAs with a very low degree of hydrolysis ($<80\%$) or low molecular weight results in coagulation and agglomeration of polymer particles and formation of polymer lumps, while using PVAs with a very high degree of hydrolysis ($>90\%$) results in unstable dispersions leading to formation of shapeless polymer bulk (Mendizabal et al., 1992). Increasing the concentration of stabiliser in general, and PVA in particular, has been found to increase its ability to stabilise the dispersion due to steric and Marangoni effects. In both simple liquid–liquid dispersion and suspension polymerisation, a smaller mean drop/particle size and sharper drop/particle size distribution have been obtained with increasing PVA concentration (Chatzi and Kiparissides, 1994; Konno et al., 1982; Lazrak et al., 1998).

It is always desired in industry to increase the output of manufacturing units at minimum cost. In suspension polymerisation processes this target is usually met by increasing the monomer hold up. However, the incorporation of more monomer destabilises the particles and also increases the possibility of thermal runaway. Therefore, a careful examination of interaction of parameters involved in suspension polymerisation reactors is required. Increase in monomer hold up enhances the dispersion viscosity and thus damps the turbulence of the system, and also increases the collision frequency of dispersed drops. All these result in larger polymer particles (Kalfas et al., 1993; Konno et al., 1982; Lazrak et al., 1998).

One important aspect of monomer-hold up can be seen in association with monomer solubility in the water phase. Water solubility of monomer is one of the factors that can affect the kinetics of the reaction and the quality of the product. When the solubility of the monomer in the aqueous phase is negligible (as it is for styrene, for example) the kinetics of suspension polymerisation can be described as similar to that of the corresponding homogeneous bulk polymerisation. However, in the case of monomers with a moderate to high water solubility, some of the monomer resides in the water phase and does not get involved in the polymerisation reaction. As polymerisation proceeds in the drops, monomer transfers from the aqueous phase into the drops to replace the monomer that has polymerised. This effect causes some deviations from the kinetics of bulk polymerisation. Kalfas et al. (1993) carried out a series of suspension homo- and copolymerisations of monomers with different water solubility. Their results showed that mass transfer limitations in suspension polymerisation of partially water-soluble monomers (methyl methacrylate, vinyl acetate and acrylonitrile) at low monomer-to-water ratios is considerable and leads to a lower final conversion in comparison with higher monomer-to-water ratios. Water solubility of monomer also causes the formation of emulsion particles in the aqueous phase. These particles are the result of the homogenous nucleation occurring in the water phase and because of segregation of radicals in these particles, the polymer formed usually has a higher molecular weight than the polymer formed in larger particles of the suspension polymerisation (Cunningham, 1999).

The variation in reaction temperature will affect the properties of both monomer and oil phases in a suspension polymerisation. A 10°C temperature increase results in a two- to threefold increase in the rate of polymerisation (Odian, 1991). The effects of temperature increase on the properties